



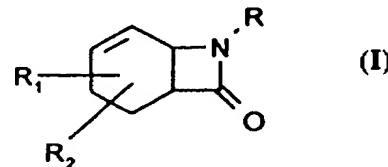
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A01N 43/44, C07D 205/12	A1	(11) International Publication Number: WO 97/10713 (43) International Publication Date: 27 March 1997 (27.03.97)
(21) International Application Number: PCT/EP96/03955 (22) International Filing Date: 10 September 1996 (10.09.96) (30) Priority Data: 2674/95 21 September 1995 (21.09.95) CH (71) Applicant (for all designated States except US): CIBA-GEIGY AG [CH/CH]; Klybeckstrasse 141, CH-4002 Basle (CH). (72) Inventor; and (75) Inventor/Applicant (for US only): ZELLER, Martin [CH/CH]; Kronengasse 7, CH-5400 Baden (CH). (74) Common Representative: CIBA-GEIGY AG; Patentabteilung, Klybeckstrasse 141, CH-4002 Basle (CH).		(81) Designated States: AU, BG, BR, BY, CA, CN, CZ, HU, IL, JP, KP, KR, MX, NZ, PL, RO, RU, SK, UA, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.

(54) Title: 7-AZABICYCLO(4.2.0)OCT-4-EN-8-ONE DERIVATES AS PLANT-MICROBICIDES

(57) Abstract

Plant-microbicidal compositions which comprise, as active ingredient, a β -lactam of the general formula (I), in which R is hydrogen; unsubstituted or substituted C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl; a group COR₃; a group COOR₄; a group SO₂R₅; and R₁ and R₂ independently of one another can be identical or different and are hydrogen; unsubstituted or substituted C₁-C₈alkyl, C₂-C₈alkenyl or C₂-C₈alkynyl; halogen; C₁-C₄alkoxy; C₂-C₄alkenyloxy; C₂-C₄alkynyloxy; or C₁-C₄alkoxycarbonyl; and R₃ is hydrogen; unsubstituted or substituted; C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl; and R₄ is unsubstituted or substituted C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl; and R₅ is unsubstituted or substituted C₁-C₈alkyl, C₃-C₈alkenyl, C₃-C₈alkynyl; amino; C₁-C₈alkylamino or C₁-C₈dialkylamino. These compositions are valuable microbicides. They can be employed in crop protection for example for controlling fungal diseases. The invention also relates to novel β -lactams of the formula (I).



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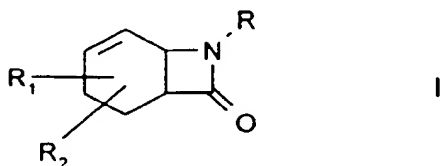
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7-AZABICYCLO(4.2.0)OCT-4-EN-8-ONE DERIVATES AS PLANT-MICROBICIDES

The present invention relates to microbicidal compositions which comprise, as active ingredient, a β -lactam of the formula I below. It relates to the preparation of the novel active ingredients and also to the preparation of the above-mentioned compositions and to the use of the active ingredients or the compositions for controlling or preventing attack of plants by phytopathogenic microorganisms, preferably fungi.

The β -lactam active ingredient has the general formula I



in which

R is hydrogen; C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by C₁-C₄alkoxy, C₁-C₄alkoxy-carbonyl, one or more halogen atoms or phenyl and in which the phenyl radical can be monosubstituted or polysubstituted by C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, C₁-C₄alkylthio, halogen, nitro, cyano or C₁-C₄alkoxy-carbonyl; a group COR₃; a group COOR₄; a group SO₂R₅; and

R₁ and R₂ independently of one another can be identical or different and are hydrogen; C₁-C₈alkyl, C₂-C₈alkenyl or C₂-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by one or more halogen atoms; halogen;

C₁-C₄alkoxy; C₂-C₄alkenyloxy; C₂-C₄alkynyloxy; or C₁-C₄alkoxycarbonyl; and

R₃ is hydrogen; C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by C₁-C₄alkoxy, C₁-C₄alkoxy-carbonyl, one or more halogen atoms or phenyl and in which the phenyl radical can be monosubstituted or polysubstituted by C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkylthio, halogen, nitro, cyano or C₁-C₄alkoxycarbonyl; and

R_4 is C_1 - C_8 alkyl, C_3 - C_8 alkenyl or C_3 - C_8 alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by C_1 - C_4 alkoxy, C_1 - C_4 alkoxycarbonyl, one or more halogen atoms or phenyl and in which the phenyl radical can be monosubstituted or polysubstituted by C_1 - C_4 alkyl, C_2 - C_4 alkenyl, C_2 - C_4 alkynyl, C_1 - C_4 haloalkyl, C_1 - C_4 haloalkoxy, C_1 - C_4 alkylthio, halogen, nitro, cyano or C_1 - C_4 alkoxycarbonyl; and

R_5 is C_1 - C_8 alkyl, C_3 - C_8 alkenyl or C_3 - C_8 alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by C_1 - C_4 alkoxy, C_1 - C_4 alkoxycarbonyl, one or more halogen atoms or phenyl and in which the phenyl radical can be monosubstituted or polysubstituted by C_1 - C_4 alkyl, C_2 - C_4 alkenyl, C_2 - C_4 alkynyl, C_1 - C_4 haloalkyl, C_1 - C_4 haloalkoxy, C_1 - C_4 alkylthio, halogen, nitro, cyano or C_1 - C_4 alkoxycarbonyl; amino, C_1 - C_8 alkylamino or C_1 - C_8 dialkylamino.

Halogen is fluorine, chlorine, bromine or iodine, preferably fluorine, chlorine or bromine.

Haloalkyl or haloalkoxy can contain identical or different halogen atoms and denote monohalogenated to perhalogenated radicals, for example $CHCl_2$, CH_2F , CCl_3 , CH_2Cl , CHF_2 , CF_3 , CH_2CH_2Br , C_2Cl_5 , $CHBrCl$ and the like.

Alkyl and alkoxy groups are straight-chain or branched, depending on the number of carbon atoms, and are, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, n-pentyl, neopentyl, sec-pentyl, tert-pentyl, n-hexyl, n-octyl and the like.

Alkenyl is to be understood as meaning straight-chain or branched alkenyl, depending on the number of carbon atoms, for example vinyl, 1-methylvinyl, allyl, 1-butenyl, isopropenyl, hexenyl.

Alkynyl is, for example, ethynyl, 1-propynyl or 1-butylnyl.

As a consequence of the presence of asymmetric carbon atoms in the compounds of the formula I, the compounds may occur in optically isomeric forms. The presence of an aliphatic $C=C$ double bond which may exist means that geometric isomerism may also occur. The formula I embraces these isomers which are possible in pure form or in the form of mixtures.

An especially preferred group of compounds of the formula I is formed by compounds in which

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R is hydrogen; C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by C₁-C₄alkoxy, C₁-C₄alkoxycarbonyl, one or more halogen atoms or phenyl and in which the phenyl radical can be substituted by C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, C₁-C₄alkylthio, halogen, nitro, cyano or C₁-C₄alkoxycarbonyl; a group COR₃; a group COOR₄; a group SO₂R₅; and

R₁ and R₂ independently of one another can be identical or different and are hydrogen, C₁-C₈alkyl, C₂-C₈alkenyl or C₂-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by one or more halogen atoms; halogen; C₁-C₄alkoxy; C₂-C₄alkenyloxy; C₂-C₄alkynyloxy; or C₁-C₄alkoxycarbonyl; and

R₃ is hydrogen, C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl; and

R₄ is C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl; and

R₅ is C₁-C₈alkyl, C₃-C₈alkenyl, C₃-C₈alkynyl, amino, C₁-C₈alkylamino or C₁-C₈dialkylamino (sub-group 1A).

Preferred compounds of the formula I are those in which

R is hydrogen; C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by C₁-C₄alkoxy, C₁-C₄alkoxycarbonyl, one or more halogen atoms or phenyl and in which the phenyl radical can be substituted by C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, C₁-C₄alkylthio, halogen, nitro, cyano or C₁-C₄alkoxycarbonyl; a group COR₃; a group COOR₄; a group SO₂R₅; and

R₁ and R₂ independently of one another can be identical or different and are hydrogen; C₁-C₈alkyl, it being possible for this alkyl radical to be unsubstituted or substituted by one or more halogen atoms; or halogen; and

R₃ is hydrogen, C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl; and

R₄ is C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl; and

R₅ is C₁-C₈alkyl, C₃-C₈alkenyl, C₃-C₈alkynyl, amino, C₁-C₈alkylamino or C₁-C₈dialkylamino (sub-group A).

Preferred within the scope of this sub-group A are those compounds of the formula I in which

R is hydrogen; C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by C₁-C₄alkoxy, C₁-C₄alkoxy-

carbonyl, one or more halogen atoms or phenyl and in which the phenyl radical can be substituted by C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, C₁-C₄alkylthio, halogen, nitro, cyano or C₁-C₄alkoxycarbonyl; a group COR₃; a group COOR₄; a group SO₂R₅; and in which R₁ and R₂ independently of one another can be identical or different and are hydrogen or C₁-C₈alkyl; R₃ is hydrogen, C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl; R₄ is C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl; and R₅ is C₁-C₈alkyl, C₃-C₈alkenyl, C₃-C₈alkynyl, amino, C₁-C₈alkylamino or C₁-C₈dialkylamino (sub-group Aa).

An especially preferred group are those compounds of the formula I in which R is hydrogen; C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by C₁-C₄alkoxy, C₁-C₄alkoxycarbonyl, one or more halogen atoms or phenyl and in which the phenyl radical can be substituted by C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, C₁-C₄alkylthio, halogen, nitro, cyano or C₁-C₄alkoxycarbonyl; a group COR₃; a group COOR₄; a group SO₂R₅; and R₁ and R₂ are hydrogen; R₃ is hydrogen, C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl; R₄ is C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl; and R₅ is C₁-C₈alkyl, C₃-C₈alkenyl, C₃-C₈alkynyl, amino, C₁-C₈alkylamino or C₁-C₈dialkylamino (sub-group Ab).

A further preferred group within the scope of the sub-group A is formed by the compounds of the formula I in which

R is hydrogen; C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by C₁-C₄alkoxy, C₁-C₄alkoxycarbonyl, one or more halogen atoms or phenyl and in which the phenyl radical can be substituted by C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, C₁-C₄alkylthio, halogen, nitro, cyano or C₁-C₄alkoxycarbonyl; a group COOR₄; and

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R_1 and R_2 independently of one another can be identical or different and are hydrogen; C_1 - C_8 alkyl, C_2 - C_8 alkenyl or C_2 - C_8 alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by one or more halogen atoms; halogen; C_1 - C_4 alkoxy; C_2 - C_4 alkenyloxy; C_2 - C_4 alkynyloxy; C_1 - C_4 alkoxycarbonyl; and R_4 is C_1 - C_8 alkyl, C_3 - C_8 alkenyl or C_3 - C_8 alkynyl (sub-group B).

Preferred within the scope of this group B are those compounds in which R is hydrogen; C_1 - C_8 alkyl, it being possible for this alkyl radical to be unsubstituted or substituted by one or more halogen atoms or phenyl and in which the phenyl radical can be substituted by C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy, halogen, nitro, cyano or C_1 - C_4 alkoxycarbonyl; a group $COOR_4$; and R_1 and R_2 independently of one another can be identical or different and are hydrogen; C_1 - C_8 alkyl, C_2 - C_8 alkenyl or C_2 - C_8 alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by one or more halogen atoms; halogen; C_1 - C_4 alkoxy; C_2 - C_4 alkenyloxy; C_2 - C_4 alkynyloxy; C_1 - C_4 alkoxycarbonyl; and R_4 is C_1 - C_8 alkyl, C_3 - C_8 alkenyl or C_3 - C_8 alkynyl (sub-group Ba).

Especially preferred are compounds of the formula I in which R is hydrogen or a group $COOR_4$; and R_1 and R_2 independently of one another can be identical or different and are hydrogen; C_1 - C_8 alkyl, C_2 - C_8 alkenyl or C_2 - C_8 alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by one or more halogen atoms; halogen; C_1 - C_4 alkoxy; C_2 - C_4 alkenyloxy; C_2 - C_4 alkynyloxy; C_1 - C_4 alkoxycarbonyl; and R_4 is C_1 - C_8 alkyl, C_3 - C_8 alkenyl or C_3 - C_8 alkynyl (sub-group Bb).

A further preferred group are those compound of the formula I in which R is hydrogen; R_1 and R_2 independently of one another can be identical or different and are hydrogen; C_1 - C_8 alkyl, C_2 - C_8 alkenyl or C_2 - C_8 alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by one or more halogen atoms; halogen; C_1 - C_4 alkoxy; C_2 - C_4 alkenyloxy; C_2 - C_4 alkynyloxy; C_1 - C_4 alkoxycarbonyl (sub-group Bc).

A specific group within the scope of the sub-group Bc are compounds of the formula I in which:

R is hydrogen; and

R₁ and R₂ independently of one another can be identical or different and are hydrogen; C₁-C₈alkyl, it being possible for this alkyl radical to be unsubstituted or substituted by one or more halogen atoms; or halogen (sub-group Bd).

Very especially preferred are compounds of the formula I in which

R is hydrogen and

R₁ and R₂ independently of one another can be identical or different and are hydrogen or C₁-C₈alkyl (sub-group Be).

7-Azabicyclo[4.2.0]oct-4-en-8-one and 3-bromo-7-azabicyclo[4.2.0]oct-4-en-8-one are known as compounds (J.H. Bateson, A.M. Quinn, R. Southgate, Tetrahedron Letters 1987, 1561 and J.R. Malpass, N.J. Tweddle, J. Chem. Soc., Chem. Commun. 1972, 1247 and J.R. Malpass, N.J. Tweddle, J. Chem. Soc., Perkin Trans. I, 1977, 874).

The use of these two compounds as agrochemically, in particular fungicidally, active ingredients has hitherto not been described in the literature.

The compounds of the formula I are, at room temperature, oils or solids which are distinguished by valuable microbicidal properties. They can be employed in the agricultural sector or related fields preventively and curatively for controlling phytopathogenic microorganisms. At low rates of concentration, the active ingredients of the formula I according to the invention are distinguished not only by outstanding microbicidal, in particular fungicidal, activity, but also by the fact that they are especially well tolerated by plants.

Surprisingly, it has now been found that the compounds of the formula I have a biocidal spectrum for controlling phytopathogenic microorganisms, in particular fungi, which is highly favourable for practical requirements. They have highly advantageous curative and preventive properties and are employed for the protection of a large number of crop plants. Using the active ingredients of the formula I, it is possible to contain or destroy the pests which are found on plants or parts of plants (fruits, flowers, foliage, stalks, tubers, roots) of a variety of crops of useful plants, and even parts of plants which are formed at a later point in

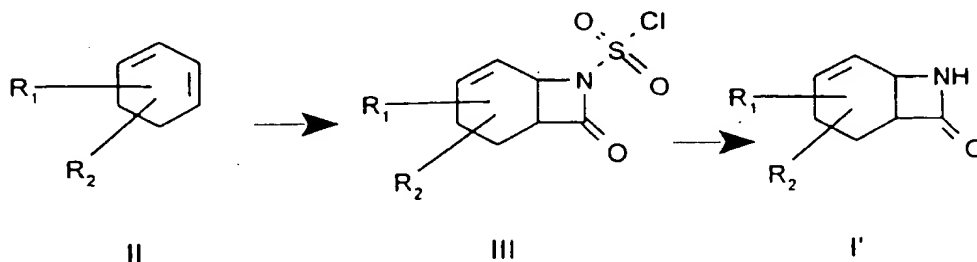
time remain unharmed by, for example, phytopathogenic fungi. Furthermore, the compounds of the formula I can be employed as a seed-dressing agent for the treatment of seed (fruits, tubers, kernels) and nursery plants as a protection against fungal infections and against soil-borne phytopathogenic fungi.

The novel active ingredients of the formula I prove active against specific genera of the fungal classes Fungi imperfecti (for example *Cercospora*), Basidiomycetes (for example *Puccinia*) and Ascomycetes (for example *Erysiphe* and *Venturia*) and, in particular, against Oomycetes (for example *Bremia*, *Plasmopara*, *Peronospora*, *Pseudoperonospora*, *Pythium* and *Phytophthora*). Thus, they are a valuable complement of the compositions for controlling phytopathogenic fungi in crop protection. Advantageously, they have both curative and preventive properties when used by the practitioner and can be employed for protecting a large number of crop plants. Using the active ingredients of the formula I, it is possible to contain or destroy the pests which are found on plants or parts of plants (fruits, flowers, foliage, stalks, tubers, roots) of a variety of crops of useful plants, and even parts of plants which are formed at a later point in time remain unharmed by, for example, phytopathogenic fungi.

The invention also relates to the novel compounds of the formula I, with the exception of the prior-art compounds 7-azabicyclo[4.2.0]oct-4-en-8-one and 3-bromo-7-azabicyclo[4.2.0]oct-4-en-8-one.

The compounds of the formula I

a) in which R is hydrogen (formula I') can be prepared by reacting a cyclohexadiene derivative of the formula II with chlorosulfonyl isocyanate and subsequently eliminating the chlorosulfonyl group



The compounds of the formula II can advantageously be reacted with chlorosulfonyl isocyanate in an indifferent diluent, such as a hydrocarbon or halohydrocarbon, for example toluene, xylene, petroleum ether, chlorobenzene, chloroform, dichloromethane, or an ether, for example dioxane, tert-butyl methyl ether, tetrahydrofuran or diethyl ether, at temperatures between -80 and +150°C, preferably between -30 and +30°C. The resulting compounds of the formula III can be isolated by evaporating the diluent or else, in a preferred variant, reacted directly to give the compounds of the formula I' by eliminating the chlorosulfonyl group. Certain reactions of compounds of the formula II with chlorosulfonyl isocyanate are described in J. Chem. Soc., Chem. Commun. 1972, 1247 and J. Chem. Soc., Perkin Trans. I 1977, 874.

In compounds of the formula III, the chlorosulfonyl group can be eliminated by reacting compounds of the formula III with water, if desired in the presence of a diluent as mentioned above (hydrocarbon, halohydrocarbon, ether), preferably in the same diluent in which the compound of the formula III has been prepared, if desired in the presence of a base, such as an alkali metal hydroxide, alkali metal carbonate, alkali metal hydrogen carbonate, alkaline earth metal hydroxide, alkaline earth metal carbonate or alkaline earth metal hydrogen carbonate, for example sodium hydroxide, potassium hydroxide, sodium hydrogen carbonate or potassium hydrogen carbonate, if desired in the presence of a stoichiometric or catalytic amount of a reducing agent, such as an alkali metal sulfite or alkaline earth metal sulfite, for example sodium sulfite, or an alkali metal iodide or alkaline earth metal iodide, for example sodium iodide, at temperatures between -30 and +100°C, preferably between 0 and +50°C. Certain reactions of compounds of the formula III with water (elimination of the chlorosulfonyl group) are described in J. Chem. Soc., Chem. Commun. 1972, 1247 and J. Chem. Soc., Perkin Trans. I 1977, 874.

b) The compounds of the formula I in which R is other than hydrogen can be prepared by reacting a compound of the formula I' above with a compound of the formula IV in which X is a leaving group, such as a halide, sulfonate or carbonate.



The compounds of the formula I' can be reacted with compounds of the formula IV in an indifferent diluent, such as a hydrocarbon, halohydrocarbon, ether or amide as mentioned above, for example N,N-dimethylformamide or N-methylpyrrolidone, or in water, if desired in the presence of an organic base, such as a tertiary amine, for example pyridine, triethylamine, diisopropylethylamine, N-methylpiperidine, N-methylmorpholine or 4-dimethylaminopyridine, or an inorganic base, such as an alkali metal carbonate or alkaline earth metal carbonate, for example sodium carbonate or potassium carbonate, or an alkali metal hydroxide or alkaline earth metal hydroxide, for example sodium hydroxide or potassium hydroxide, or a metal hydride or metal amide, for example sodium hydride or lithium diisopropylamide, or in the presence of mixtures of these bases; and, if desired, in the presence of a phase transfer catalyst, such as a quaternary ammonium compound, for example tetrabutyl ammonium chloride, tetrabutyl ammonium bromide or tetrabutyl ammonium hydroxide, trimethylbenzyl ammonium chloride, trimethylbenzyl ammonium bromide or trimethylbenzyl ammonium hydroxide at temperatures between -120 and +150°C, preferably between 0 and +50°C.

The invention also relates to the use of the compositions in the agricultural sector or in related fields.

Moreover, the present invention also includes the preparation of these compositions, which comprises intimately mixing the active substance with one or more substances or substance groups described in the present publication. Also included is a method for treating plants, which comprises applying the novel compounds of the formula I, or the novel compositions.

Target crops for the use in crop protection disclosed herein are within the scope of the present invention for example the following plant species: cereals (wheat, barley, rye, oats, rice, maize, sorghum and related species); beet (sugar and fodder beet); pomaceous fruit, stone fruit and soft fruit (apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries and blackberries); leguminous plants (beans, lentils, peas, soya beans); oil crops (oilseed rape, mustard, poppies, olives, sunflowers, coconut, castor, cocoa, peanuts); cucurbits (pumpkin, cucumbers, melons); fibre plants (cotton, flax, hemp, jute); citrus fruit (oranges, lemons, grapefruit, mandarines); vegetables (spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, bell peppers); the laurel family (avocado,

Cinnamoniun, camphor), or plants such as tobacco, nuts, coffee, sugar cane, tea, pepper, grapevines, hops, the plantain family, latex plants, ornamentals and flowers.

Active ingredients of the formula I are normally used in the form of compositions and can be applied to the area or plant to be treated simultaneously with other active ingredients or in succession. These other active ingredients can be fertilizers, trace element mediators or other preparations which affect plant growth. Others which can be used are selective herbicides or insecticides, fungicides, bactericides, nematocides, molluscicides or mixtures of a plurality of these preparations together with, if appropriate, other carriers, surfactants or application-enhancing additives conventionally used in the art of formulation.

Suitable carriers and surfactants can be solid or liquid and are the substances expediently used in the art of formulation, for example natural or regenerated mineral substances, solvents, dispersants, wetting agents, tackifiers, thickeners, binders or fertilizers.

A preferred method for applying an active ingredient of the formula I or of an agrochemical composition which comprises at least one of these active ingredients is application to the foliage (foliar application). Frequency and rate of application depend on the risk of infestation with the pathogen in question. The compounds of the formula I can also be applied to seed kernels (coating), either by soaking the kernels in a liquid preparation of the active ingredient or by coating them with a solid preparation.

The compounds of the formula I are employed in pure form or, preferably, together with the auxiliaries conventionally used in the art of formulation. To this end, they are expediently processed in a known manner to give, for example, emulsion concentrates, spreadable pastes, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granules or encapsulations, for example in polymeric substances. The methods of application, such as spraying, atomizing, dusting, scattering, brushing on or pouring, are selected to suit the intended aims and the prevailing circumstances, as is the type of the compositions.

Favourable rates of application are generally at from 1 g to 2 kg of active substance (a.s.) per hectare (ha), preferably 10 g to 1 kg, in particular 25 g to 750 g of a.s./ha. When used as

seed-dressing products, dosages of from 0.001 g to 1.0 g of active ingredient are advantageously used per kg of seed.

The formulations, i.e. the compositions, preparations or products comprising the active ingredients of the formula I and, if desired, a solid or liquid additive, are prepared in a known manner, for example by intimately mixing and/or grinding the active ingredient with extenders, such as solvents, solid carriers and, if desired, surface-active compounds (surfactants).

The following are suitable as solvents: aromatic hydrocarbons, preferably the fractions C₈ to C₁₂, such as xylene mixtures or substituted naphthalenes, phthalic esters, such as isobutyl or dioctyl phthalate, aliphatic hydrocarbons, such as cyclohexane or paraffins, alcohols and glycols and also ethers and esters, such as ethanol, ethylene glycol, ethylene glycol mono-methyl ester or ethylene glycol monoethyl ester, ketones, such as cyclohexanone, strongly polar solvents, such as N-methylpyrrolidone, dimethyl sulfoxide or dimethylformamide, and also free or epoxidized vegetable oils, such as epoxidized coconut oil or soya oil. Solid carriers which are used, for example for dusts and dispersible powders are, as a rule, ground natural minerals, such as calcite, talc, kaolin, montmorillonite or attapulgite. To improve the physical properties, highly-disperse silica or highly-disperse absorptive polymers may also be added. Suitable particulate absorptive carriers for granules are porous types, such as pumice, brick grit, sepiolite or bentonite, suitable non-sorptive carrier materials are, for example, calcite or sand. In addition, a large number of pregranulated materials of inorganic or organic nature, such as dolomite or comminuted plant residues, may be used.

Depending on the nature of the active ingredient of the formula I to be formulated, suitable surface-active compounds are non-ionic, cationic and/or anionic surfactants which have good emulsifying, dispersing and wetting properties. Surfactants are also to be understood as meaning surfactant mixtures.

Suitable anionic surfactants can be both so-called water-soluble soaps and water-soluble synthetic surface-active compounds.

Examples of non-ionic surfactants which may be mentioned are nonylphenol polyethoxy-ethanols, castor oil polyglycol ether, polypropylene/polyethylene oxide adducts, tributyl-phenoxy polyethylene-ethanol, polyethylene glycol and octylphenoxy polyethoxyethanol.

Fatty acid esters of polyethylenesorbitan, such as polyoxyethylenesorbitan trioleate are furthermore also suitable.

The cationic surfactants are mainly quaternary ammonium salts which have, as N-substituent, at least one alkyl radical having 8 to 22 C atoms and, as further substituents, lower, free or halogenated alkyl, benzyl or lower hydroxyalkyl radicals.

Other surfactants conventionally used in the art of formulation are known to those skilled in the art or can be found in the relevant specialist literature.

As a rule, the agrochemical preparations comprise 0.01 to 99 per cent by weight, in particular 0.1 to 95 per cent by weight, of active ingredient of the formula I, 99.99 to 1 per cent by weight, in particular 99.9 to 5 per cent by weight, of a solid or liquid additive and 0 to 25 per cent by weight, in particular 0.1 to 25 per cent by weight, of a surfactant.

While concentrated compositions are more preferred as commercially available goods, the end user uses, as a rule, dilute compositions.

The compositions can also comprise other additives such as stabilizers, antifoams, viscosity regulators, binders, tackifiers, and also fertilizers and other active ingredients to achieve specific effects.

The examples which follow illustrate the invention described above without imposing any limitation to its scope. Temperatures are given in degrees Celsius.

Preparation examples of the compounds of the formula I

H-1.1 : Preparation of 7-azabicyclo[4.2.0]oct-4-en-8-one

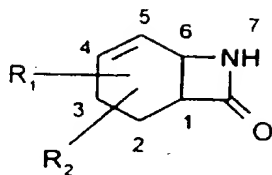
A solution of 55 ml of 1,3-cyclohexadiene in 400 ml of dichloromethane is added dropwise in the course of 25 minutes to a solution of 50 ml of chlorosulfonyl isocyanate in 400 ml of

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dichloromethane. During this process, the internal temperature is kept at +20°C by means of cooling using an ice-bath. After the addition has ended, the reaction mixture is stirred for 25 minutes at room temperature. The resulting mixture, most of which is composed of a solution of N-chlorosulfonyl-7-azabicyclo[4.2.0]oct-4-en-8-one in dichloromethane, is added dropwise to a mechanically stirred solution of 169 g of potassium hydrogen carbonate and 7.3 g of sodium sulfite in 1.2 l of water. Stirring of the resulting emulsion is continued for a further 45 minutes. 500 ml of water are added. The mixture is extracted using diethyl ether. The organic phase is washed using saturated sodium chloride solution, dried over magnesium sulfate and evaporated to dryness. This gives 7-azabicyclo[4.2.0]oct-4-en-8-one, which can be purified by chromatography on silica gel using methyl acetate/n-hexane 2:1 or by recrystallization from methyl acetate/n-hexane. M.p. 74-76°C.

The compounds listed in Table 1 are prepared analogously.

Table 1



Comp. No.	R ₁	R ₂	Physical data
1.1	H	H	m.p. 74-76°C
1.2	3-methyl	H	
1.3	2-methyl	H	
1.4	3-ethyl	H	
1.5	2-ethyl	H	
1.6	4-methyl	H	
1.7	1-methyl	H	
1.8	5-methyl	H	
1.9	6-methyl	H	
1.10	3-methyl	3-methyl	
1.11	2-methyl	2-methyl	
1.12	3-tert-butyl	H	
1.13	2-tert-butyl	H	
1.14	3-methyl	2-methyl	
1.15	4-methyl	1-methyl	
1.16	5-methyl	6-methyl	
1.17	6-methyl	1-methyl	
1.18	5-methyl	4-methyl	
1.19	3-allyl	H	
1.20	2-allyl	H	
1.21	3-propargyl	H	
1.22	2-propargyl	H	
1.23	3-methoxy	H	
1.24	2-methoxy	H	

1.25	3-allyloxy	H
1.26	2-allyloxy	H
1.27	3-propargyloxy	H
1.28	2-propargyloxy	H
1.29	4-chloro	H
1.30	1-chloro	H
1.31	2-chloro	H
1.32	4-chloro	1-chloro
1.33	5-trifluoromethyl	H
1.34	6-trifluoromethyl	H
1.35	3-methoxycarbonyl	H
1.36	2-methoxycarbonyl	H
1.37	4-methoxycarbonyl	H
1.38	1-methoxycarbonyl	H
1.39	5-methoxycarbonyl	H
1.40	6-methoxycarbonyl	H

H-2.1 : Preparation of N-methyl-7-azabicyclo[4.2.0]oct-4-en-8-one

0.52 g of tetrabutyl ammonium bromide, 2.8 g of methyl iodide and 1.1 g of pulverulent potassium hydroxide are added to a solution of 2 g of 7-azabicyclo[4.2.0]oct-4-en-8-one in 30 ml of tetrahydrofuran. The reaction mixture is stirred for 6 hours at room temperature. It is then diluted with 100 ml of water. It is extracted using diethyl ether. The organic phase is washed using saturated sodium chloride solution, dried over magnesium sulfate and evaporated to dryness. This gives N-methyl-7-azabicyclo[4.2.0]oct-4-en-8-one as an oil which can be purified by chromatography on silica gel using ethyl acetate.

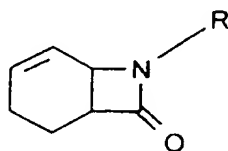
H-2.32 : Preparation of N-tert-butoxycarbonyl-7-azabicyclo[4.2.0]oct-4-en-8-one

A mixture of 6 g of 7-azabicyclo[4.2.0]oct-4-en-8-one (Comp. 1.1), 21.3 g of di-tert-butyl dicarbonate, 6 g of 4-dimethylaminopyridine and 3.8 ml of triethylamine in 100 ml of dichloromethane is stirred for 6 hours at room temperature under a nitrogen atmosphere. The reaction mixture is introduced into 2N hydrochloric acid. It is extracted using dichloromethane. The organic phase is washed with water, dried over magnesium sulfate and

evaporated to dryness. This gives N-tert-butoxycarbonyl-7-azabicyclo[4.2.0]oct-4-en-8-one as an oil which can be purified by chromatography on silica gel.

The compounds listed in Table 2 are prepared analogously.

Table 2



Comp. No.	R	Physical data
2.1	methyl	oil
2.2	ethyl	
2.3	allyl	oil
2.4	propargyl	
2.5	isopropyl	
2.6	n-propyl	
2.7	n-butyl	
2.8	2,2,2-trifluoroethyl	
2.9	methoxycarbonyl-methyl	
2.10	2-methoxy-ethyl	
2.11	methoxymethyl	
2.12	benzyl	oil
2.13	p-nitrobenzyl	
2.14	m-trifluoromethylbenzyl	
2.15	p-methoxybenzyl	
2.16	m-methoxybenzyl	
2.17	o-chlorobenzyl	
2.18	m-chlorobenzyl	
2.19	p-chlorobenzyl	oil
2.20	p-cyanobenzyl	
2.21	p-(ethoxycarbonyl)-benzyl	
2.22	p-methylthiobenzyl	

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2.23	p-trifluoromethoxybenzyl	
2.24	p-difluoromethoxybenzyl	
2.25	1-phenylethyl	
2.26	2-phenylethyl	
2.27	3-phenyl-propen-yl	
2.28	-CO-CH ₃	m.p. 33-35°C
2.29	-CO-CH ₂ -CH ₃	
2.30	-CO-C(CH ₃) ₃	
2.31	-CO-CH=CH(CH ₃)	
2.32	-COO-C(CH ₃) ₃	oil
2.33	-COO-CH ₃	
2.34	-COO-CH ₂ -CH ₃	
2.35	-COO-CH(CH ₃) ₂	
2.36	-COO-C(CH ₃) ₂ -CH ₂ -CH ₃	oil
2.37	-COO-CH ₂ -CH=CH ₂	oil
2.38	-SO ₂ -CH ₃	
2.39	-SO ₂ -CH ₂ -CH ₃	
2.40	-SO ₂ -NH ₂	
2.41	-SO ₂ -NH-CH ₃	
2.42	-SO ₂ -NH-CH ₂ -CH ₃	
2.43	-SO ₂ -N(CH ₃) ₂	
2.44	-SO ₂ -N(CH ₃)-CH ₂ -CH ₃	
2.45	-SO ₂ -N(CH ₂ -CH ₃) ₂	
2.46	3,4-dichlorobenzyl	
2.47	2,4-dichlorobenzyl	
2.48	2,5-dichlorobenzyl	
2.49	2,4,6-trimethylbenzyl	
2.50	4-methyl-3-nitrobenzyl	
2.51	2,3,4,5,6-pentafluorobenzyl	
2.52	2-methoxy-5-nitrobenzyl	
2.53	4-methoxycarbonylbenzyl	
2.54	3,4,5-trimethoxybenzyl	
2.55	2-fluoro-4-trifluoromethylbenzyl	

2.56	-CO-phenyl	m.p. 61-63°C
2.57	-CO-(4-chlorophenyl)	
2.58	-CO-(4-fluorophenyl)	
2.59	-CO-(4-nitrophenyl)	
2.60	-CO-(3-trifluoromethylphenyl)	
2.61	-CO-(4-methoxyphenyl)	
2.62	-CO-(4-methylphenyl)	
2.63	-CO-(2,4-dichlorophenyl)	
2.64	-CO-(2-chloro-4-nitrophenyl)	
2.65	-CO-(3,4-dimethylphenyl)	
2.66	-CO-(2,4,6-trichlorophenyl)	
2.67	-CO-(2,3,4,5,6-pentafluoro-phenyl)	
2.68	-CO-CH=CH-phenyl	
2.69	-CO-CH ₂ -phenyl	
2.70	$\text{—COO—CH}_2\text{—}\equiv\text{CH}$	
2.71	-COO-phenyl	
2.72	-COO-CH ₂ -phenyl	
2.73	-COO-CH ₂ -(4-methylphenyl)	
2.74	-COO-CH ₂ -(4-chlorophenyl)	
2.75	-COO-CH ₂ -CH ₂ -Cl	
2.76	-SO ₂ -phenyl	
2.77	-SO ₂ -(2-chlorophenyl)	
2.78	-SO ₂ -(3-chlorophenyl)	
2.79	-SO ₂ -(4-chlorophenyl)	
2.80	-SO ₂ -(4-methylphenyl)	m.p. 95-96°C
2.81	-SO ₂ -(4-bromophenyl)	
2.82	-SO ₂ -(4-nitrophenyl)	
2.83	-SO ₂ -(3-trifluoromethylphenyl)	
2.84	-SO ₂ -(2,4-dichlorophenyl)	
2.85	-SO ₂ -CH ₂ -phenyl	

Formulation examples of active ingredients of the formula I (% = per cent by weight)F-1 : Wettable powders

	a)	b)	c)
Active ingredient of Tables 1 and 2	25 %	50 %	75 %
Sodium lignosulfonate	5 %	5 %	--
Sodium lauryl sulfate	3 %	--	5 %
Sodium diisobutyl-naphthalenesulfonate	--	6 %	10 %
Octylphenol polyethylene glycol ether (7-8 mol of ethylene oxide)	--	2 %	--
Highly-disperse silica	5 %	10 %	10 %
Kaolin	62 %	27 %	--

The active ingredient is mixed thoroughly with the additives and ground thoroughly in a suitable mill. This gives wettable powders which can be diluted with water to give suspensions of any desired concentration.

F-2 : Emulsion concentrate

Active ingredient of Tables 1 and 2	10 %
Octylphenol polyethylene glycol ether (4-5 mol of ethylene oxide)	3 %
Calcium dodecylbenzenesulfonate	3 %
Castor oil glycol ether (35 mol of ethylene oxide)	4 %
Cyclohexanone	34 %
Xylene mixture	50 %

Emulsions of any desired concentration can be prepared from this concentrate by diluting with water.

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F-3 : Dusts

	a)	b)
Active ingredient of Tables 1 and 2	5 %	8 %
Talc	95 %	--
Kaolin	--	92 %

Ready-to-use dusts are obtained by mixing the active ingredient with the carrier and grinding the mixture in a suitable mill.

F-4 : Extruder granules

Active ingredient of Tables 1 and 2	10 %
Sodium lignosulfonate	2 %
Carboxymethylcellulose	1 %
Kaolin	87 %

The active ingredient is mixed with the additives, and the mixture is ground and moistened with water. This mixture is extruded and subsequently dried in a stream of air.

F-5 : Coated granules

Active ingredient of Tables 1 and 2	3 %
Polyethylene glycol (MW 200)	3 %
Kaolin	94 %

In a mixer, the finely ground active ingredient is applied uniformly to the kaolin which has been moistened with polyethylene glycol. This gives dust-free coated granules.

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F-6 : Suspension concentrate

Active ingredient of Tables 1 and 2	40 %
Ethylene glycol	10 %
Nonylphenol polyethylene glycol ether (15 mol of ethylene oxide)	6 %
Sodium lignosulfonate	10 %
Carboxymethylcellulose	1 %
37 % aqueous formaldehyde solution	0.2 %
Silicone oil in the form of a 75 % aqueous emulsion	0.8 %
Water	32 %

The finely ground active ingredient is mixed intimately with the additives. This gives a suspension concentrate from which suspensions of any desired concentration can be prepared by dilution with water.

Biological ExamplesB-1 : Activity against Plasmopara viticola on grapevines

a) Residual-protective action

Grapevine seedlings in the 4-5-leaf stage are sprayed with a spray mixture prepared with wettable powder of the active ingredient (0.02 % of active substance). After 24 hours, the treated plants are infected with a sporangia suspension of the fungus. After incubation for 6 days at a relative atmospheric humidity of 95-100 % and 20°C, the fungus infestation is assessed.

b) Residual-curative action

Grapevine seedlings in the 4-5-leaf stage are infected with a sporangia suspension of the fungus. After incubation for 24 hours in a humid chamber at a relative atmospheric humidity of 95-100 % and 20°C, the infected plants are dried and sprayed with a spray mixture prepared with wettable powder of the active ingredient (0.02 % of active substance). After the spray coating has dried on, the treated plants are returned to the humid chamber. The fungus infestation is assessed 6 days after infection.

Compounds of Tables 1 and 2 exhibit very good fungicidal activity against *Plasmopara viticola* on grapevines. The active ingredient No. 1.1, inter alia, resulted in complete

suppression of fungus infestation (residual infestation 0 to 5 %). Untreated, but infected control plants, in contrast, show a *Plasmopara* infestation of 100 %.

B-2 : Activity against *Phytophthora* on tomato plants

a) Residual-protective action

Tomato plants are grown for 3 weeks and then sprayed with a spray mixture prepared with wettable powder of the active ingredient (0.02 % of active substance). After 48 hours, the treated plants are infected with a sporangia suspension of the fungus. The fungus infestation is assessed after incubation of the infected plants for 4 days at a relative atmospheric humidity of 90-100 % and 20°C.

b) Systemic action

Tomato plants are grown for 3 weeks, and a spray mixture prepared with wettable powder of the active ingredient (0.02 % of active substance based on the soil volume) is then added to them. Care is taken that the spray mixture does not come into contact with the aerial parts of the plants. After 96 hours, the treated plants are infected with a sporangia suspension of the fungus. The fungus infestation is assessed after incubation of the infected plants for 4 days at a relative atmospheric humidity of 90-100 % and 20°C.

Compounds of Tables 1 and 2 (for example 2.1, 2.12, 2.19, 2.28, 2.32, 2.56 and 2.80) exhibit a sustained activity (fungus infestation less than 20 %). The compound 1.1 prevents infestation virtually completely (0 to 5 % infestation). Untreated, but infected control plants, by contrast, showed a *Phytophthora* infestation of 100 %.

B-3 : Activity against *Phytophthora* on potato plants

a) Residual-protective action

Potato plants (variety Bintje) 2-3 weeks old are sprayed with a spray mixture prepared with wettable powder of the active ingredient (0.02 % of active substance). After 48 hours, the treated plants are sprayed with a sporangia suspension of the fungus. The fungus infestation is assessed after incubation of the infected plants for 4 days at a relative atmospheric humidity of 90-100 % and 20°C.

b) Systemic action

A spray mixture prepared with wettable powder of the active ingredient (0.02 % of active substance based on the soil volume) is added to potato plants (variety Bintje) which are

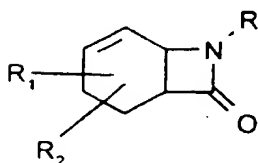
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2-3 weeks old. Care is taken that the spray mixture does not come into contact with the aerial parts of the plants. After 96 hours, the treated plants are infected with a sporangia suspension of the fungus. The fungus infestation is assessed after incubation of the infected plants for 4 days at a relative atmospheric humidity of 90-100 % and 20°C.

Compounds of Tables 1 and 2 exhibit a sustained activity (fungus infestation less than 20 %). The compound 1.1 prevents infestation virtually completely (0 to 5 % infestation). Untreated, but infected control plants, in contrast, exhibited a *Phytophthora* infestation of 100 %.

WHAT IS CLAIMED IS:

1. A plant-microbicidal composition comprising at least one compound of the formula I



in which

R is hydrogen; C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by C₁-C₄alkoxy, C₁-C₄alkoxycarbonyl, one or more halogen atoms or phenyl and in which the phenyl radical can be monosubstituted or polysubstituted by C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, C₁-C₄alkylthio, halogen, nitro, cyano or C₁-C₄alkoxycarbonyl; a group COR₃; a group COOR₄; a group SO₂R₅; and

R₁ and R₂ independently of one another can be identical or different and are hydrogen; C₁-C₈alkyl, C₂-C₈alkenyl or C₂-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by one or more halogen atoms; halogen; C₁-C₄alkoxy; C₂-C₄alkenyloxy; C₂-C₄alkynyloxy; or C₁-C₄alkoxycarbonyl; and

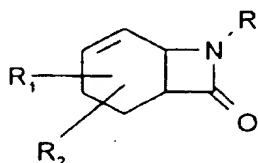
R₃ is hydrogen; C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by C₁-C₄alkoxy, C₁-C₄alkoxycarbonyl, one or more halogen atoms or phenyl and in which the phenyl radical can be monosubstituted or polysubstituted by C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkylthio, halogen, nitro, cyano or C₁-C₄alkoxycarbonyl; and

R₄ is C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by C₁-C₄alkoxy, C₁-C₄alkoxycarbonyl, one or more halogen atoms or phenyl and in which the phenyl radical can be monosubstituted or polysubstituted by C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkylthio, halogen, nitro, cyano or C₁-C₄alkoxycarbonyl; and

R₅ is C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by C₁-C₄alkoxy, C₁-C₄alkoxycarbonyl, one

or more halogen atoms or phenyl and in which the phenyl radical can be monosubstituted or polysubstituted by C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkylthio, halogen, nitro, cyano or C₁-C₄alkoxycarbonyl; amino, C₁-C₈alkylamino or C₁-C₈dialkylamino, together with a suitable carrier material.

2. A plant-microbicidal composition according to claim 1 comprising at least one compound of the formula I



in which

R is hydrogen; C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by C₁-C₄alkoxy, C₁-C₄alkoxycarbonyl, one or more halogen atoms or phenyl and in which the phenyl radical can be substituted by C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, C₁-C₄alkylthio, halogen, nitro, cyano or C₁-C₄alkoxycarbonyl; a group COR₃; a group COOR₄; a group SO₂R₅; and R₁ and R₂ independently of one another can be identical or different and are hydrogen; C₁-C₈alkyl, C₂-C₈alkenyl or C₂-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by one or more halogen atoms; halogen; C₁-C₄alkoxy; C₂-C₄alkenyloxy; C₂-C₄alkynyloxy; or C₁-C₄alkoxycarbonyl; and R₃ is hydrogen, C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl; and R₄ is C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl; and R₅ is C₁-C₈alkyl, C₃-C₈alkenyl, C₃-C₈alkynyl, amino, C₁-C₈alkylamino or C₁-C₈dialkylamino, together with a suitable carrier material.

3. A plant-microbicidal composition according to claim 2 in which

R_1 and R_2 independently of one another can be identical or different and are hydrogen; C_1 - C_8 alkyl, it being possible for this alkyl radical to be unsubstituted or substituted by one or more halogen atoms; or halogen.

4. A plant-microbicidal composition according to claim 3 in which R_1 and R_2 independently of one another can be identical or different and are hydrogen or C_1 - C_8 alkyl.
5. A plant-microbicidal composition according to claim 4 in which R_1 and R_2 are hydrogen.
6. A plant-microbicidal composition according to claim 2 in which R is hydrogen; C_1 - C_8 alkyl, C_3 - C_8 alkenyl or C_3 - C_8 alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by C_1 - C_4 alkoxy, C_1 - C_4 alkoxy-carbonyl, one or more halogen atoms or phenyl and in which the phenyl radical can be substituted by C_1 - C_4 alkyl, C_2 - C_4 alkenyl, C_2 - C_4 alkynyl, C_1 - C_4 haloalkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy, C_1 - C_4 alkylthio, halogen, nitro, cyano or C_1 - C_4 alkoxycarbonyl; or a group $COOR_4$.
7. A plant-microbicidal composition according to claim 6 in which R is hydrogen; C_1 - C_8 alkyl, it being possible for this alkyl radical to be unsubstituted or substituted by one or more halogen atoms or phenyl and in which the phenyl radical can be substituted by C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy, halogen, nitro, cyano or C_1 - C_4 alkoxycarbonyl; or a group $COOR_4$.
8. A plant-microbicidal composition according to claim 7 in which R is hydrogen or a group $COOR_4$.
9. A plant-microbicidal composition according to claim 8 in which R is hydrogen.
10. A plant-microbicidal composition according to claim 9 in which

R_1 and R_2 independently of one another can be identical or different and are hydrogen; C_1 - C_8 alkyl, it being possible for this alkyl radical to be unsubstituted or substituted by one or more halogen atoms; or halogen.

11. A plant-microbicidal composition according to claim 10 in which R_1 and R_2 independently of one another can be identical or different and are hydrogen or C_1 - C_8 alkyl.

12. A plant-microbicidal composition according to claim 2 comprising the compound 7-azabicyclo[4.2.0]oct-4-en-8-one.

13. A method for controlling or preventing infestation of plants by microorganisms, which comprises applying plant-microbicidal compositions according to claim 1, comprising, as active ingredient, a compound of the formula I, to the plant, to the parts of the plant or to the plant substrate.

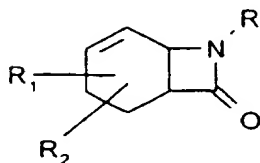
14. A method according to claim 13, which comprises applying plant-microbicidal compositions according to claims 2 to 12.

15. A method according to claim 13, wherein phytopathogenic fungi are controlled.

16. A method according to claim 15, wherein Oomycetes are controlled.

17. The use of a compound of the formula I as microbicide.

18. A compound of the formula I



in which

R is hydrogen; C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by C₁-C₄alkoxy, C₁-C₄alkoxycarbonyl, one or more halogen atoms or phenyl and in which the phenyl radical can be monosubstituted or polysubstituted by C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, C₁-C₄alkylthio, halogen, nitro, cyano or C₁-C₄alkoxycarbonyl; a group COR₃; a group COOR₄; a group SO₂R₅; and

R₁ and R₂ independently of one another can be identical or different and are hydrogen; C₁-C₈alkyl, C₂-C₈alkenyl or C₂-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by one or more halogen atoms; halogen; C₁-C₄alkoxy; C₂-C₄alkenyloxy; C₂-C₄alkynyloxy; or C₁-C₄alkoxycarbonyl; and

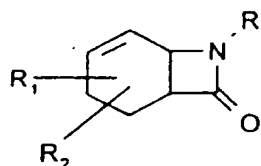
R₃ is hydrogen; C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by C₁-C₄alkoxy, C₁-C₄alkoxycarbonyl, one or more halogen atoms or phenyl and in which the phenyl radical can be monosubstituted or polysubstituted by C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkylthio, halogen, nitro, cyano or C₁-C₄alkoxycarbonyl; and

R₄ is C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by C₁-C₄alkoxy, C₁-C₄alkoxycarbonyl, one or more halogen atoms or phenyl and in which the phenyl radical can be monosubstituted or polysubstituted by C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkylthio, halogen, nitro, cyano or C₁-C₄alkoxycarbonyl; and

R₅ is C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by C₁-C₄alkoxy, C₁-C₄alkoxycarbonyl, one or more halogen atoms or phenyl and in which the phenyl radical can be monosubstituted or polysubstituted by C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₄haloalkyl, C₁-C₄haloalkoxy, C₁-C₄alkylthio, halogen, nitro, cyano or C₁-C₄alkoxycarbonyl; amino, C₁-C₈alkylamino or C₁-C₈dialkylamino; with the exception of the compounds 7-azabicyclo[4.2.0]oct-4-en-8-one and 3-bromo-7-azabicyclo[4.2.0]oct-4-en-8-one.

19. A compound of the formula I according to claim 18

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in which

R is hydrogen; C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by C₁-C₄alkoxy, C₁-C₄alkoxycarbonyl, one or more halogen atoms or phenyl and in which the phenyl radical can be substituted by C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, C₁-C₄alkylthio, halogen, nitro, cyano or C₁-C₄alkoxycarbonyl; a group COR₃; a group COOR₄; a group SO₂R₅; and

R₁ and R₂ independently of one another can be identical or different and are hydrogen; C₁-C₈alkyl, C₂-C₈alkenyl or C₂-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by one or more halogen atoms; halogen; C₁-C₄alkoxy; C₂-C₄alkenyloxy; C₂-C₄alkynyloxy; or C₁-C₄alkoxycarbonyl; and R₃ is hydrogen, C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl; and

R₄ is C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl; and

R₅ is C₁-C₈alkyl, C₃-C₈alkenyl, C₃-C₈alkynyl, amino, C₁-C₈alkylamino or C₁-C₈dialkylamino.

20. A compound of the formula I according to claim 19 in which

R₁ and R₂ independently of one another can be identical or different and are hydrogen; C₁-C₈alkyl, it being possible for this alkyl radical to be unsubstituted or substituted by one or more halogen atoms; or halogen.

21. A compound according to claim 20 in which

R₁ and R₂ independently of one another can be identical or different and are hydrogen or C₁-C₈alkyl.

22. A compound according to claim 21 in which

R₁ and R₂ are hydrogen.

23. A compound according to claim 19 in which
R is hydrogen; C₁-C₈alkyl, C₃-C₈alkenyl or C₃-C₈alkynyl, it being possible for these alkyl, alkenyl or alkynyl radicals to be unsubstituted or substituted by C₁-C₄alkoxy, C₁-C₄alkoxy-carbonyl, one or more halogen atoms or phenyl and in which the phenyl radical can be substituted by C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, C₁-C₄alkylthio, halogen, nitro, cyano or C₁-C₄alkoxycarbonyl; or a group COOR₄.
24. A compound according to claim 23 in which
R is hydrogen; C₁-C₈alkyl, it being possible for this alkyl radical to be unsubstituted or substituted by one or more halogen atoms or phenyl and in which the phenyl radical can be substituted by C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, halogen, nitro, cyano or C₁-C₄alkoxycarbonyl; or a group COOR₄.
25. A compound according to claim 24, in which
R is hydrogen or a group COOR₄.
26. A compound according to claim 25 in which
R is hydrogen.
27. A compound according to claim 26 in which
R₁ and R₂ independently of one another can be identical or different and are hydrogen; C₁-C₈alkyl, it being possible for this alkyl radical to be unsubstituted or substituted by one or more halogen atoms; or halogen.
28. A compound according to claim 27 in which
R₁ and R₂ independently of one another can be identical or different and are hydrogen or C₁-C₈alkyl.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 96/03955

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A01N43/44 C07D205/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A01N C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 001 271 (BASF AG.) 4 April 1979 see page 18; claims ---	1,18
A	WO,A,87 07270 (CHEVRON RESEARCH CO.) 3 December 1987 see claims ---	1,18
A	WO,A,94 27444 (CROP GENETICS INTERNATIONAL CORPORATION) 8 December 1994 see page 5; claims ---	1,18
A	EP,A,0 232 017 (THE UPJOHN COMPANY) 12 August 1987 see page 53; claims ---	18
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

14 November 1996

Date of mailing of the international search report

27.11.96

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Chouly, J

INTERNATIONAL SEARCH REPORT

Initial Application No.

PCT/EP 96/03955

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	<p>JOURNAL OF THE CHEMICAL SOCIETY, PERKIN TRANSACTIONS 1, no. 10, 1991, LETCHWORTH GB, pages 2399-2405, XP002018529 J.H. BATESON ET AL.: "Olivanic acid analogues." see page 2400, formula 20a; page 2403, right column, paragraph 5</p> <p style="text-align: center;">---</p>	18
A	<p>JOURNAL OF THE CHEMICAL SOCIETY CHEMICAL COMMUNICATIONS, no. 22, 22 November 1972, pages 1247-1248, XP002018530 J.R. MALPASS ET AL.: "Reaction of chlorosulphonyl isocyanate with cyclic dienes . Evidence for a true dipole in 2+2 addition" cited in the application see the whole article, especially formula 2, page 1248</p> <p style="text-align: center;">-----</p>	18

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International Application No

PCT/EP 96/03955

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